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Effects of temperature, triazole and hot-pressing on the performance of TiO_2 photoanode in a solid-state photoelectrochemical cell

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ABSTRACT

The photocurrent of hydrogen generating solid-state photoelectrochemical cell utilising a polybenzimidazole proton-conducting membrane and gaseous anode reactants has been enhanced by operation at higher temperatures. With a bias of 0 V for example, photocurrent increased from 15 to 30 $\mu A/cm^2$ on moving from 25 °C to 45 °C. The increase in photocurrent, which was limited by the dehydration of the cell, was shown to have contribution from improved electrode kinetics. Modification of TiO_2 surface with triazole, a conjugated heterocyclic compound, led to significant increase in photocurrent up to 4 fold increase at 0 V and 25 °C. This was attributed to improved separation of photogenerated charge carriers, as confirmed by correspondingly increased carrier lifetimes from 50 ns to 90 ns for triazole-modified TiO_2. Assembly of the photoelectrochemical cell by hot-pressing induced a ˜0.3 eV red shift in optical absorption edge of TiO_2, in agreement with a shift of its valence band maximum to higher binding energy.

1. Introduction

Efficient direct conversion of solar to chemical energy will help make solar energy an alternative to fossil fuels. Among the many possibilities is the conversion of CO_2 to gaseous and liquid fuel [1–5], and hydrogen production from aqueous solutions [6–10]. The latter is sometimes accomplished with organic additives like methanol in order to reduce charge carrier recombination and boost solar to chemical conversion efficiency [10]. In these mentioned processes, there are basically two approaches: photocatalytic conversion and use of photoelectrochemical (PEC) cells. Both approaches rely on absorption of photon energy by a semiconductor photocatalyst to generate electrons and holes. In photocatalytic conversion, the chemical processes leading to product formation take place on the surface of photocatalyst nanoparticles suspended in a solvent. Since both the photogenerated holes and electrons are active in the same region, complications can arise when only one particular reaction is desirable, for example reduction to yield H_2 or hydrocarbons. Photocatalytic conversion may have side reactions that limit the efficiency of the preferred reactions [4,5] and/or lead to production of mixtures of oxidising and reducing gases [7–9] (e.g. O_2 and H_2). The second approach is based on the use of PEC cells and allows reduction and oxidation reactions to take place at two different and spatially separated electrodes. Here, it is possible to not only separate the electrode products but also to modify the conditions at one electrode in order to enhance the half reaction there without negatively affecting the half reaction at the other electrode [11].

The majority of PEC hydrogen generation studies involve the use of aqueous electrolyte as both the electrolyte and the photoanode reactants, and among them are very few attempts to separate the two half reactions compartments with a proton conducting membrane [11–13] as is the case in polymer electrolyte membrane (PEM) electrolysis. Recently, we have been investigating the use of gaseous reactants at the photoanode of a PEC hydrogen generating cell, similar in design to a PEM water electrolysis cell [14]. This approach is expected to benefit from the advantages of using a solid polymer over aqueous electrolytes, namely, operation at higher temperatures in order to improve electrode kinetics and reduce the thermodynamic energy requirement for electrolysis [15], pressurising the system to produce compressed H_2 directly [16] and absence of gas bubbles which can impede reactions at the electrode surfaces [17]. The use of a gaseous mixture of ethanol and water

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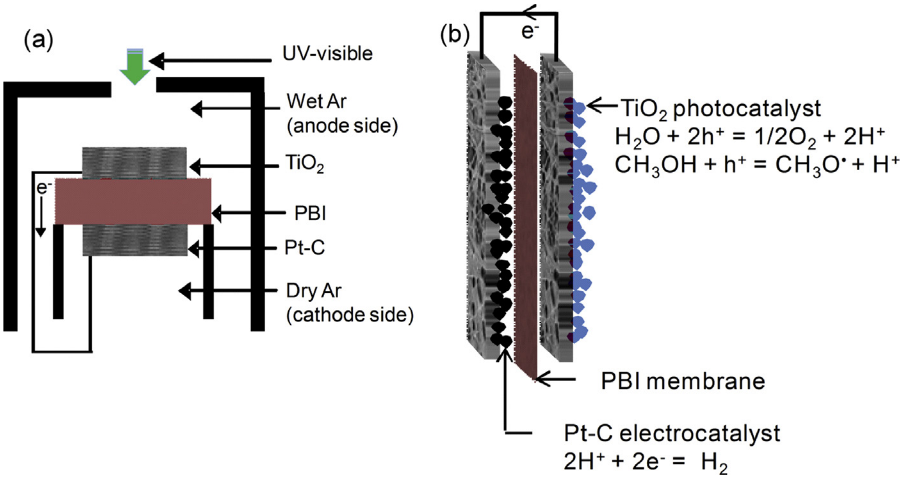

Fig. 1. (a) Schematic of a PEC cell on a ProboStat^{TM} sample holder, (b) an enlarged view of the cell indicating some of the reactions going on at the electrodes. The methoxy radical produced at the photoanode can undergo further reaction to produce more H^+, electrons and CO_2 [12].

for PEC hydrogen generation with a PEM electrolyser type cell has been reported [18], while a similar cell design has been utilised for PEC degradation of organics in air [19,20]. However, there is little or insufficient information on the effects of surface characteristics and temperature on the electrode and electrolyte processes of such a system.

In this work, we study the effect of temperature on the performance of a solid-state PEC hydrogen generating cell comprising a TiO_2 photoanode, Pt-C cathode and an H_3PO_4-doped polybenzimidazole (PBI) proton conducting membrane. The effects of hot-pressing on the optical properties of TiO_2, and triazole-TiO_2 conjugation on the photocurrent of the assembled cell, are also analysed.

2. Experimental

Nafion® perfluorinated resin solution (20 wt. %) and 1*H*-1,2,3-triazole (97%, hereafter referred to as triazole) were obtained from Sigma-Aldrich. Carbon paper (190 µm thick) and platinum coated carbon, Pt-C (Pt/Vulcan XC-72R, 10 wt. % Pt) were obtained from Quintech, Germany. PBI membrane (40 µm in dry condition) was sourced from Danish Power Systems. It was acid-doped by immersing the dry membrane in 85% H_3PO_4 for at least 5 days to ensure high doping level. All dilutions were made with isopropanol.

The procedures for preparation of TiO_2 photoanode (Degussa P25) and Pt-C cathode layers on carbon paper support, and PEC experiments are the same as in our earlier publication in an all solid-state PEC hydrogen generating cell [14], except for a few modifications. The photoanode layer was either TiO_2 with 20 wt.% Nafion® (n-TiO_2/C) or 20 wt.% of Nafion® + triazole (nt-TiO_2/C). The Nafion® + triazole solution was obtained by stirring their mixture (weight ratio of 7:3 in favour of Nafion®) for 1 h. The Pt-C electrocatalyst was saturated with H_3PO_4 by dripping 20 µl of 10.6 wt.% H_3PO_4 aqueous solution. H_3PO_4 is needed to maintain good proton conductivity at higher temperatures when the proton conductivity of Nafion® drops off due to dehydration [21–23]. That was also one of the reasons for adding triazole to the anode side [21]. H_3PO_4 was intentionally not used in the anode side to avoid introduction of particulates which may interfere with light absorption and electronic conductivity. The photocatalyst and Pt-C loadings were each approximately 1.5 mg/cm^2.

The catalyst layers were placed on opposite side of the PBI membrane and hot-pressed at 160 °C for 4 min under a pressure of 35 kg/cm^2 to get the PEC cell [11]. Non-hot-pressed TiO_2/organic samples, nt-TiO_2/G (nt-TiO_2 dropcast on glass), and n-TiO_2/G (n-TiO_2 dropcast on glass) were also prepared for optical studies. We have recently studied the performances of PEC cells assembled with and without hot-pressing, and found that the non-hot-pressed cell – membrane electrode assembly implemented by using Nafion as adhesive gave a superior performance, despite possessing a larger cell resistance. The superior performance was attributed to better hydration of the non-hot-pressed cell [14]. However, the latter is not used in this work because dehydration at higher temperatures affects it strongly and masks any positive effect of increasing temperature on its photocurrent.

Diffuse reflectance spectroscopy (DRS) was carried out with a Thermo Scientific EVO-600 UV–visspectrophotometer. The band gap energies were thereafter determined using standard Kubelka-Munk and Tauc treatment of the DRS spectra. Photoluminescence (PL) measurements were performed using a 325 nm line of cw He-Cd laser (10 mW) for excitation and fibre-optic spectrometer (Ocean Optics, USB4000) for analysis. Temperature-dependent PL was performed using a closed-cycle He-cryostat operating in the range 10–300 K. Time-resolved photoluminescence (TRPL) was carried out at 10 K by employing a 372 nm wavelength 50 ps-pulsed laser (PicoQuant, 2 mW@40 MHz). The spectral region of interest was filtered out from the total PL signal using an imaging spectrograph (HORIBA Jobin Yvon, iHR320), and then the corresponding PL decay transient was analysed by time-correlated single photon counting system (PicoQuant, TimeHarp200) with overall time resolution of ~50 ps.

X-ray photoelectron spectroscopy (XPS) was performed on a KRATOS AXIS ULTRA^{DLD} using monochromatic Al Kα radiation ($h\nu$ = 1486.6 eV). The spectra were acquired at zero angle of emission, $\theta = 0°$ (normal emission) with the lenses in hybrid mode (i.e. both the magnetic and electrostatic lenses were used). The samples were not conducting, and charge neutralisation was applied to compensate for the charging effects. This was achieved with the use of low energy electrons driven by a magnetic field towards the sample surface. In practice, overcompensation takes place and this manifests in a shift of all peaks to lower binding energies. The spectra were energy corrected by initially placing the Ti 2p position at 458.8 eV [24] and then by correcting the C 1s spectra of hot-pressed samples so that their *C–F* peaks coincide with those of the non-hot-pressed ones.

The Pt/C electrode functioned as both the counter and reference electrode in a standard two-electrode configuration. Any effects from the cathode (hydrogen electrode) have been neglected, thus assuming that the impact from cathode kinetics and double layer